

Radiocarbon as a Reactive Tracer for Tracking Permanent CO₂ Storage in Basaltic Rock

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Infrastructure for CCS
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Presentation Outline

- Benefit to the Program
- Project Overview
- The CarbFix Project, Iceland
- Monitoring & Verification Results
- Accomplishments to Date
- Summary

Benefit to the Program

- The goal of the project is to develop and test novel geochemical tracer techniques for quantitative monitoring, verification and accounting of stored CO₂. These techniques contribute to the Carbon Storage Program's effort of ensuring 99% storage permanence.

Benefit to the Program cont.

- We are developing and testing the feasibility of carbon-14 (^{14}C) as a reactive tracer for quantitative monitoring and accounting of geological CO_2 storage.
- ^{14}C is the only feasible tracer tagging the CO_2 molecule itself
- Our approach provides a surveying tool for **dissolved** or **chemically transformed** CO_2 .
- The technology, when successfully demonstrated, will provide an improvement over current monitoring practices.

Project Overview:

Goals and Objectives

- Monitoring subsurface CO₂ transport with trifluormethylsulphur pentafluoride (SF₅CF₃) and sulfurhexafluoride (SF₆).
- Testing carbon-14 (¹⁴C) as a reactive tracer for geochemical reactions (including mineral carbonation) caused by CO₂ injection at the CarbFix pilot injection site, Iceland.
- Drilling small diameter coreholes into injection zone for mineral carbonation study on core samples.
- Quantify the extent of mineral carbonation in the CarbFix basalt CO₂ storage reservoir.
- This research leads to advanced monitoring and accounting of geologic CO₂ storage.

Technical Status – CarbFix Project



- ~200 tons of CO₂ injected in January 2012
- ~73 tons of CO₂/H₂S were injected starting June 2012

CarbFix partners:

- Orkuveita Reykjavíkur (Reykjavik Energy), Iceland
- University of Iceland, Iceland
- CNRS, University of Toulouse, France
- Columbia University, New York, USA

Target zone for CO₂ sequestration identified at 400-800 m depth

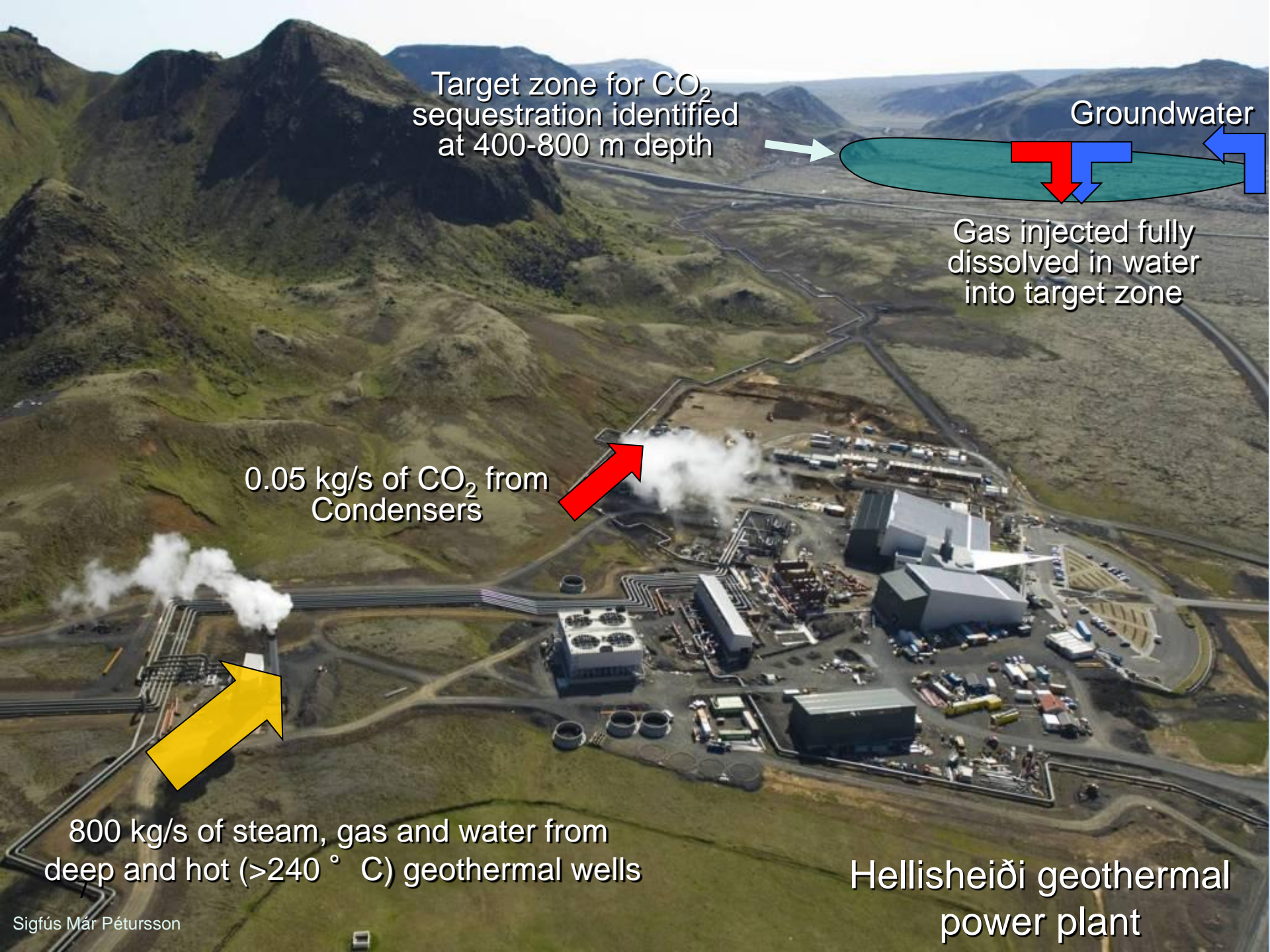
Groundwater

Gas injected fully dissolved in water into target zone

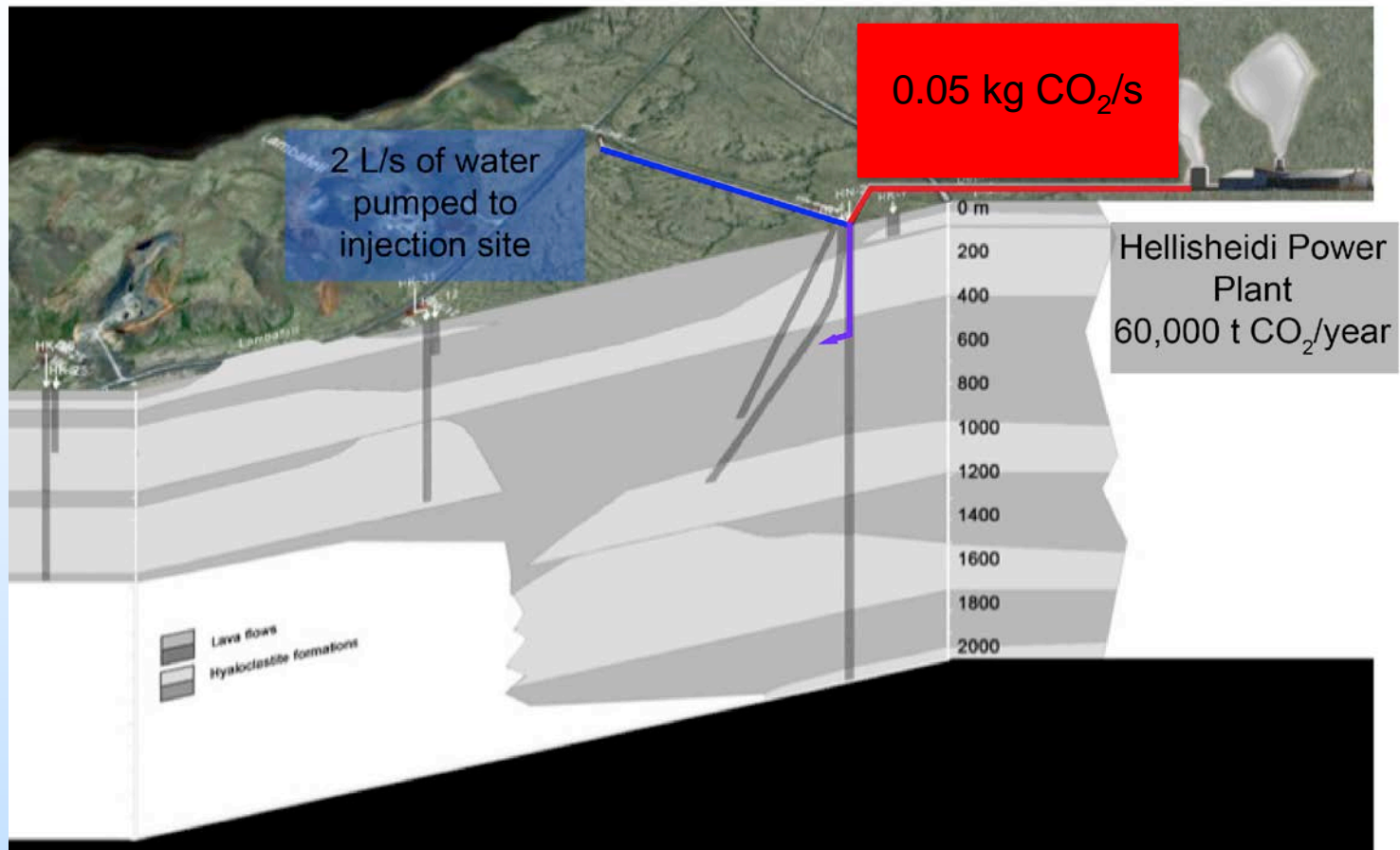
0.05 kg/s of CO₂ from Condensers

800 kg/s of steam, gas and water from deep and hot (>240 ° C) geothermal wells

Hellisheiði geothermal power plant

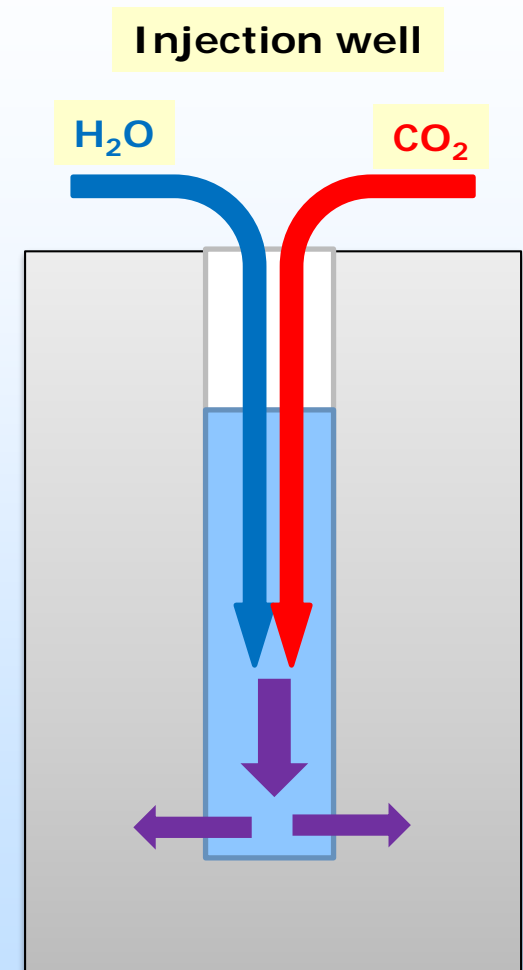
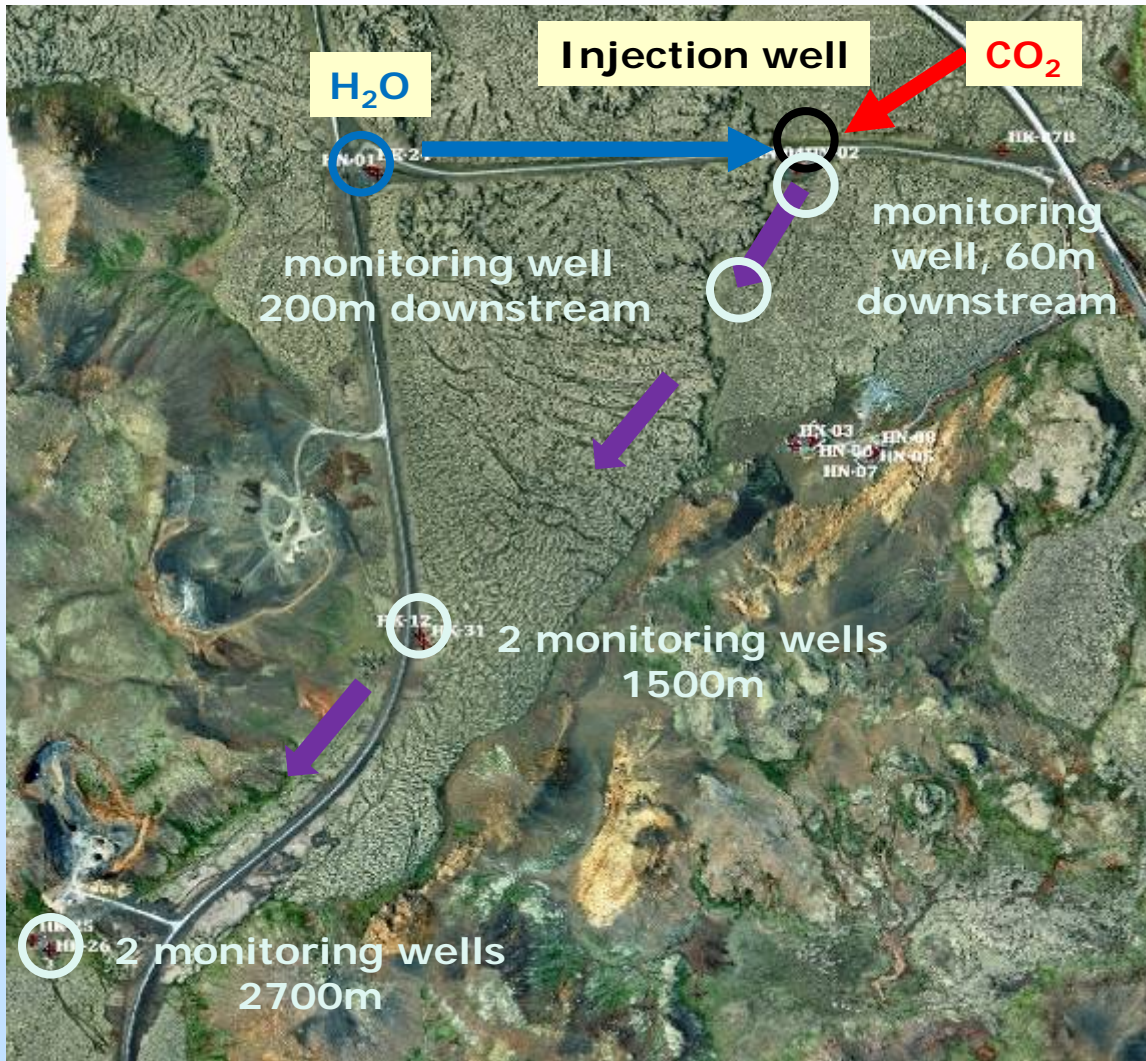


Injection Process

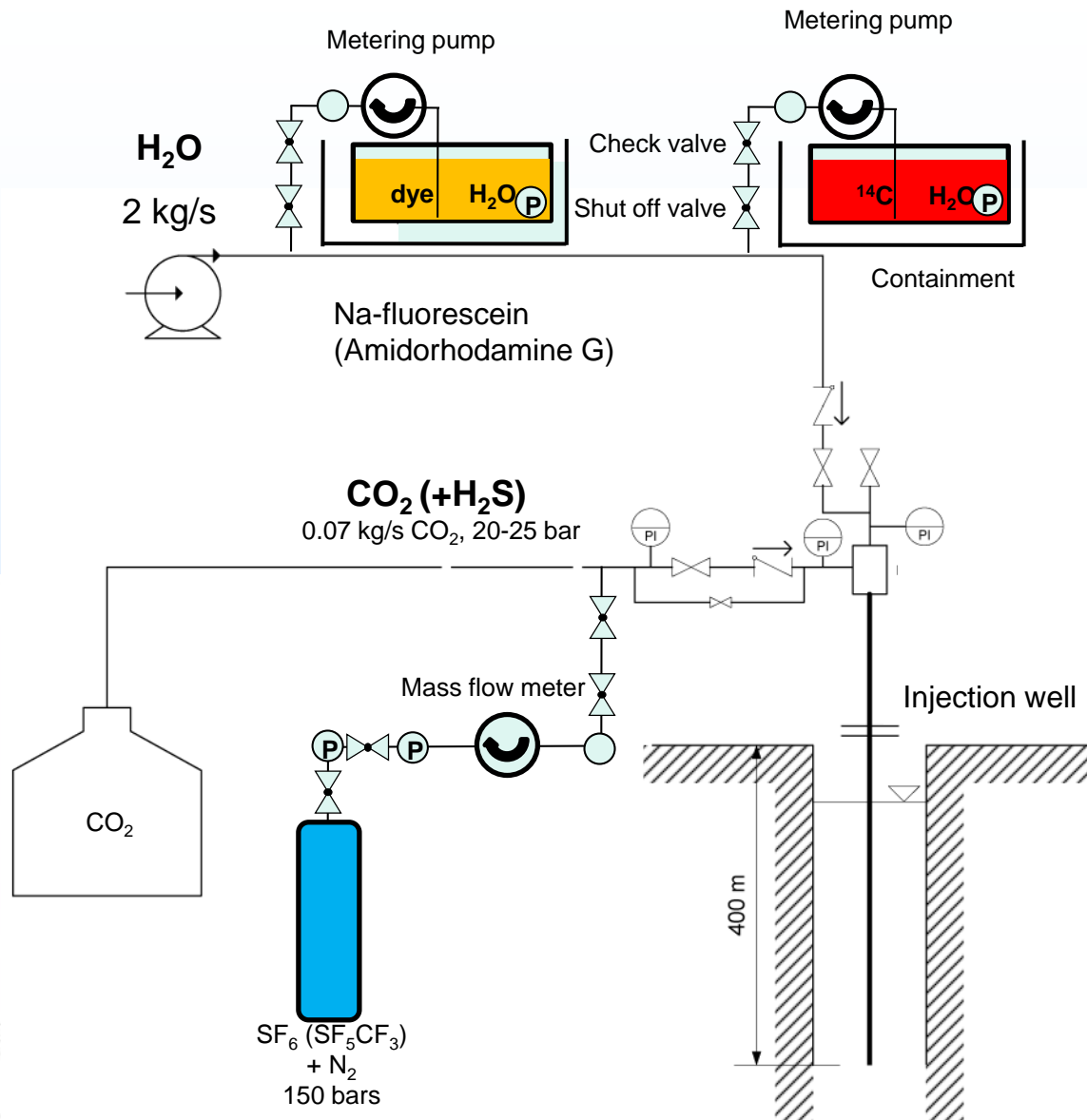


distance between injection and first monitoring well is 60 m at injection interval depth

Monitoring Infrastructure



Tracer injection system



Injection Phases

Phase I

pure CO₂ injection of ~200 tons
(January – February 2012)
SF₆ & ¹⁴C as tracers

Phase II

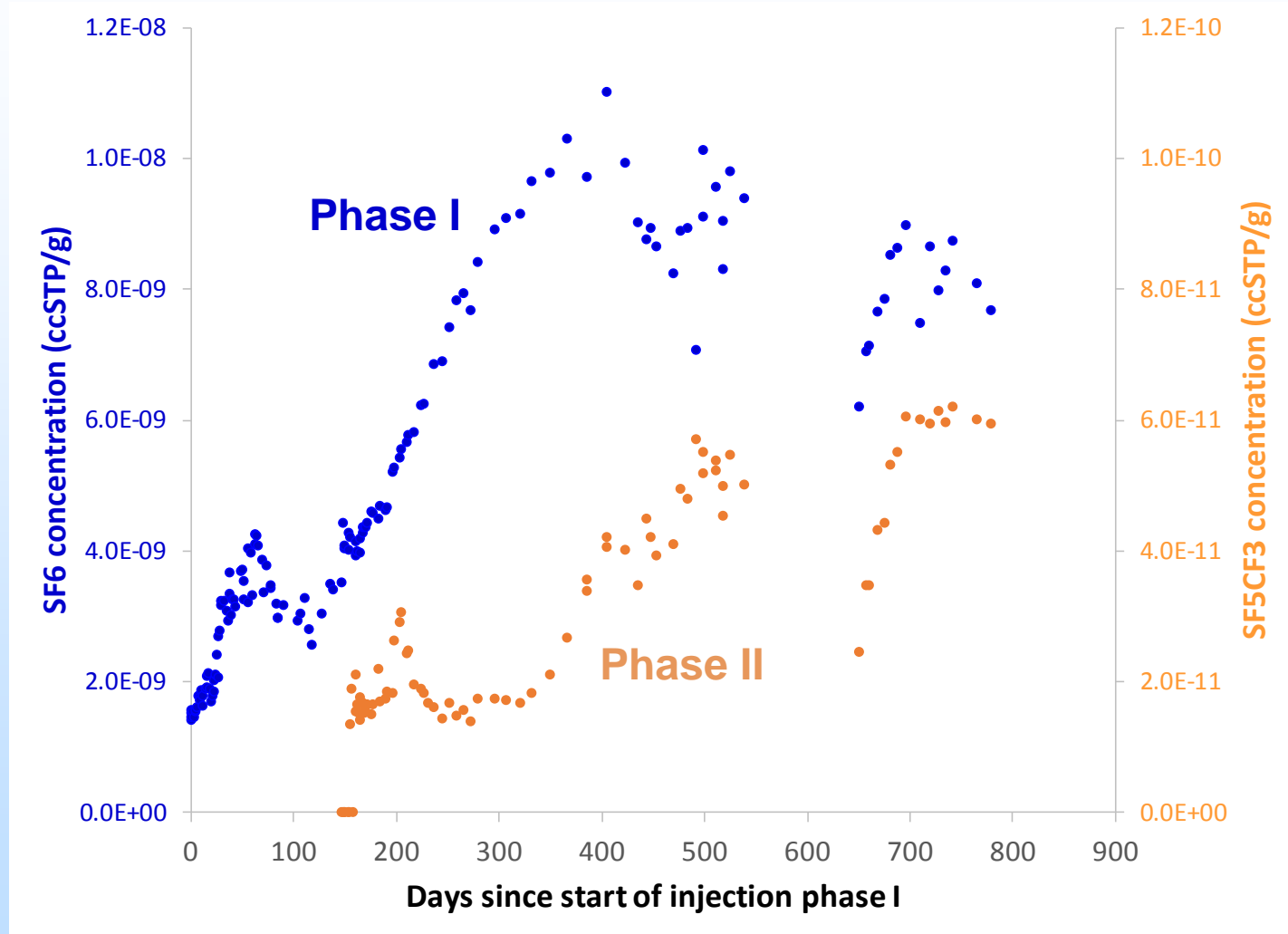
CO₂+H₂S injection (80% CO₂, 20% H₂S)
~73 tons of CO₂ (June 2012 – March 2013)
(stopped because of (bio)-clogging)
SF₅CF₃, AmidRhod G & ¹⁴C

Phase III (outside of this project)

CO₂+H₂S injection (70% CO₂, 30% H₂S)
~10000 tons of CO₂ (2014)
SF₅CF₃, sulfonate, iodide & ¹⁴C

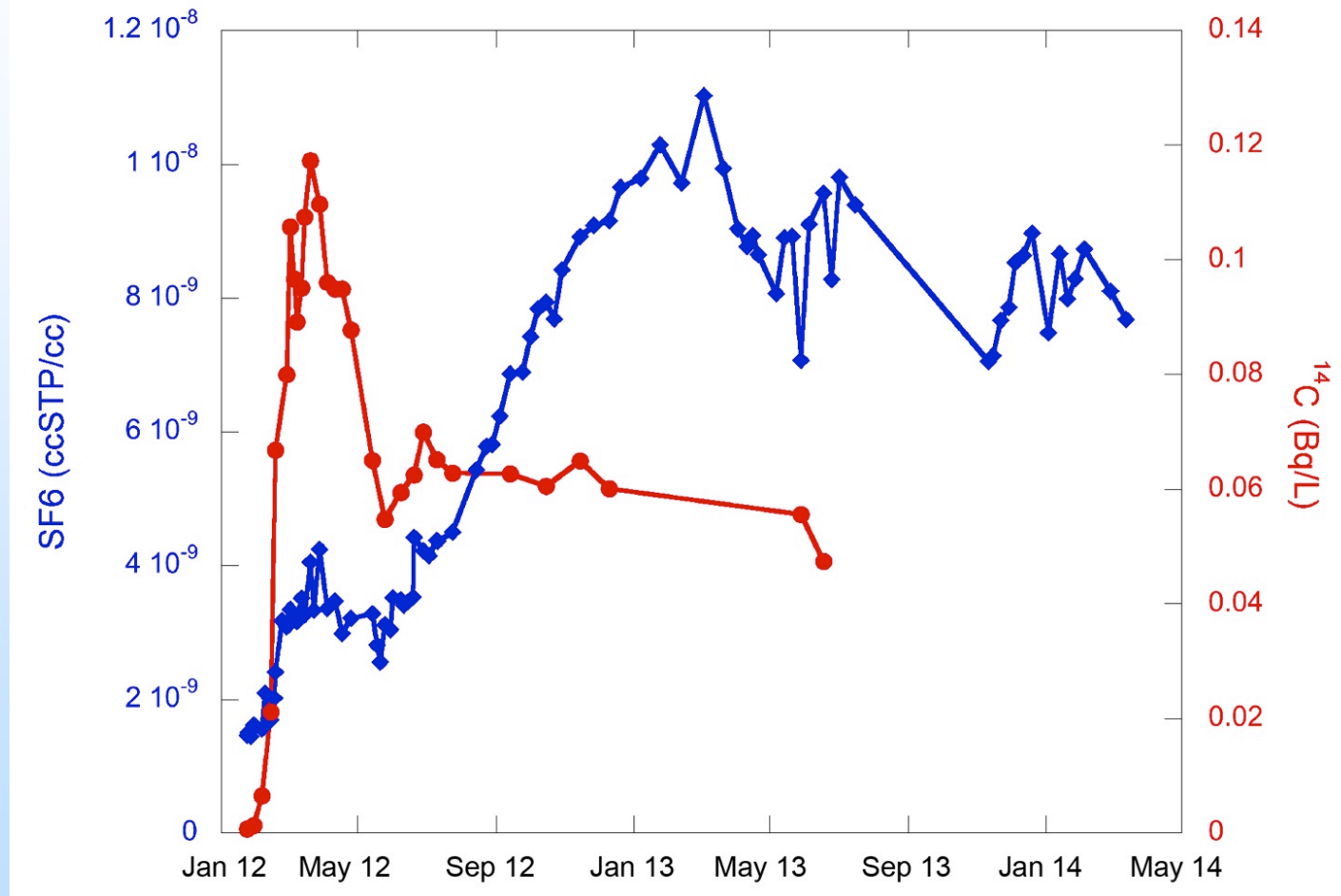
Phase I & II: SF₆ & SF₅CF₃ Monitoring Results

- Goal: Monitor advective and dispersive transport of injected solution

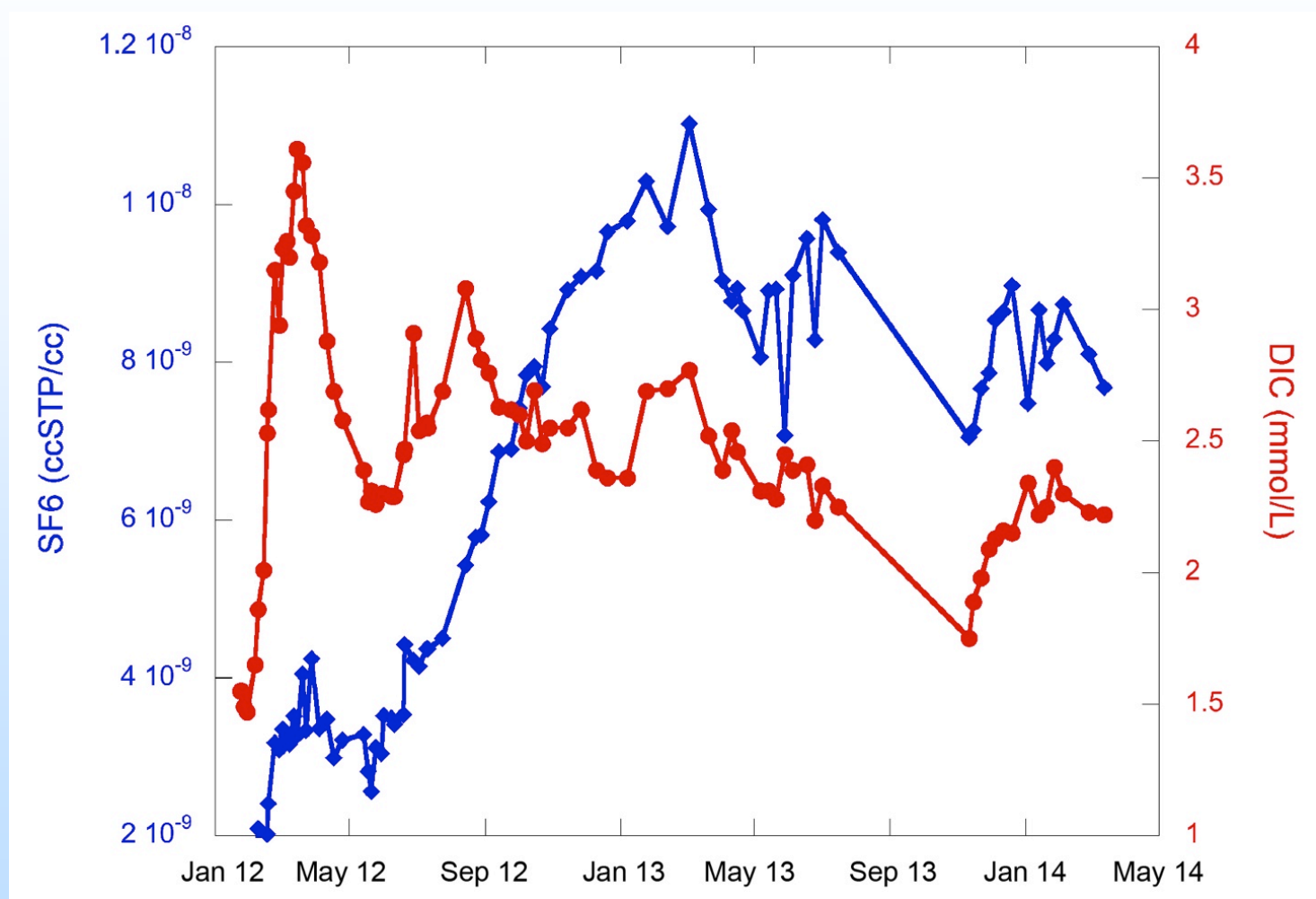


Phase I: ^{14}C Monitoring

- Goal: Monitor CO_2 -fluid-rock reactions (carbon mass balance)



Phase I: Dissolved Inorganic Carbon Monitoring



Carbon Mass Balance

1. Calculating mixing between injected solution and reservoir fluid using SF_6

$$[SF_6]_i = X[SF_6]_{IS} + (1 - X)[SF_6]_{BW}$$

2. Calculating theoretical dissolved inorganic carbon concentration (DIC_{mix}) due to pure mixing in the reservoir

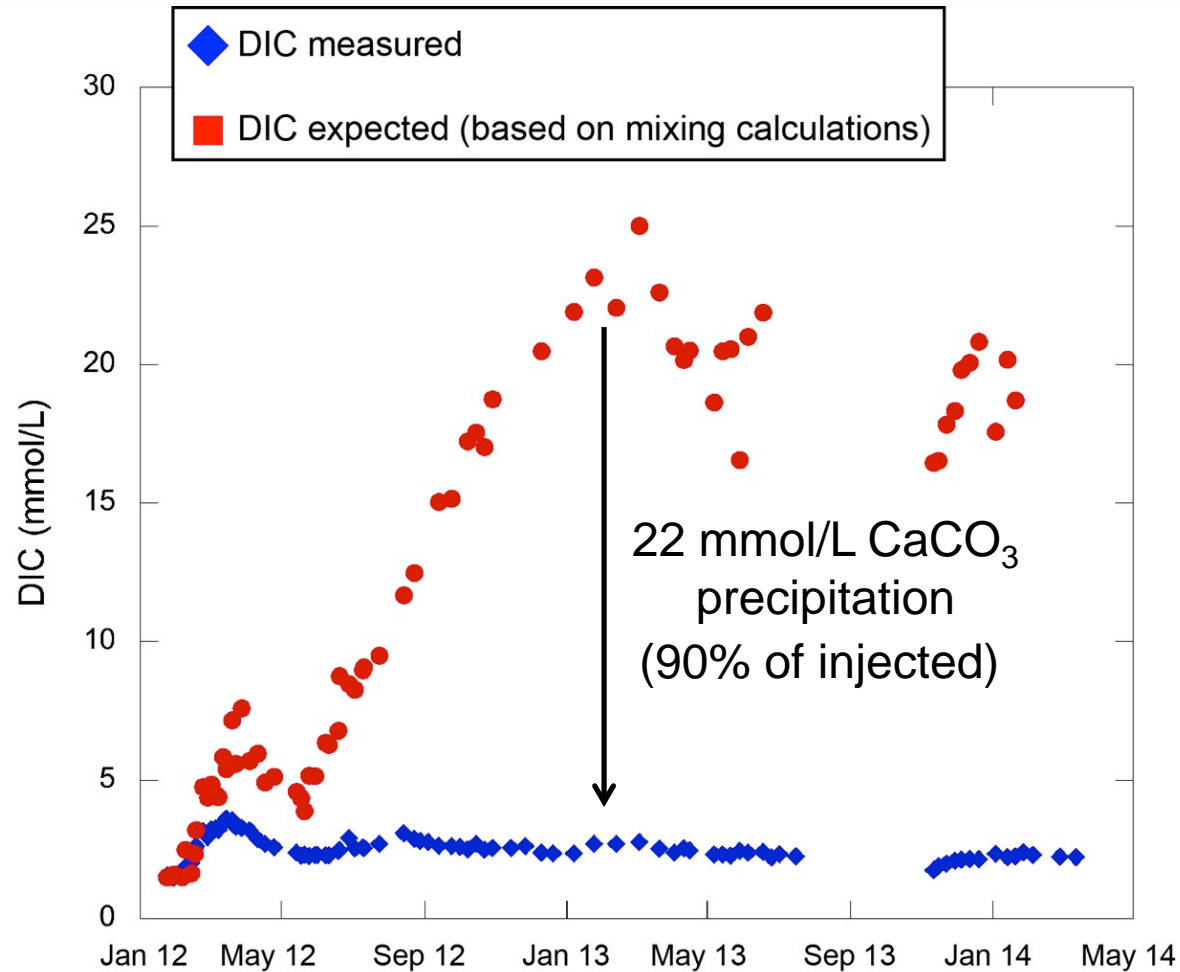
$$DIC_{mix} = X_{SF_6} \cdot DIC_{IS} + (1 - X_{SF_6}) \cdot DIC_{BW}$$

3. Calculating difference between measured and theoretical DIC

$$\Delta DIC = DIC_{sample} - DIC_{mix}$$

Carbon Mass Balance

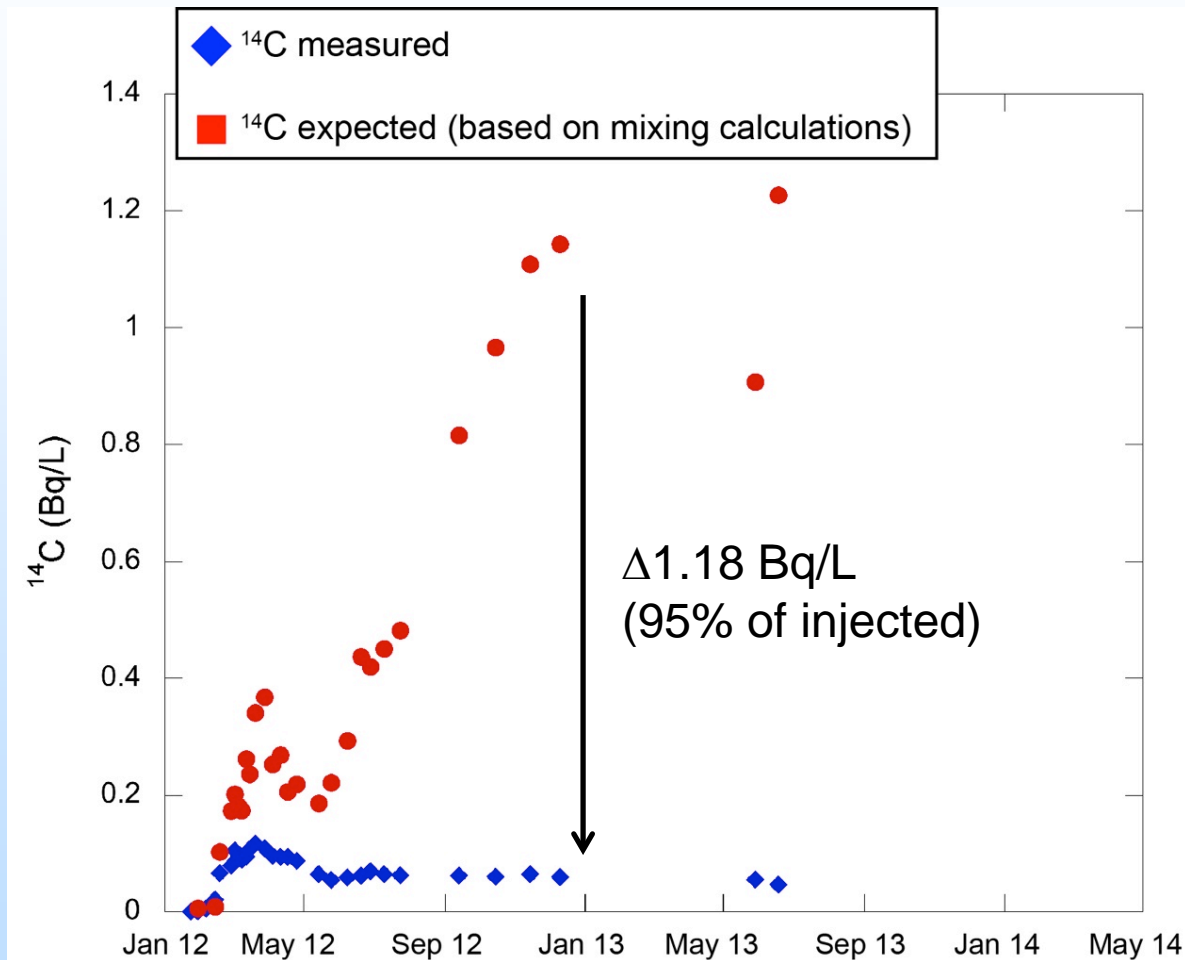
expected vs. measured DIC concentration



- Data gap from Aug 2013 – Dec 2013 because of submersible pump failure

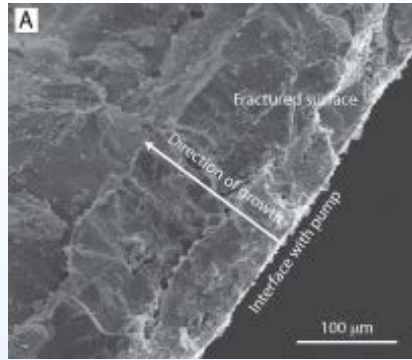
^{14}C Mass Balance

expected vs measured ^{14}C concentration



- Data gap from Aug 2013 – Dec 2013 because of submersible pump failure

Carbonate Precipitation in Reservoir



SEM image of precipitate sample including interface with submersible pump



EDX map of precipitate sample, showing Ca, Fe, Si distribution

Dideriksen K (unpublished data)

Sample ID	Name	$^{14}\text{C}/^{12}\text{C}$ Fraction modern
2013-5	2013-5-carbonate	7.82 ± 0.05
2013-6	2013-6-carbonate	7.48 ± 0.08

Average $^{14}\text{C}/^{12}\text{C}$ in last 10 water samples: 7.93 ± 0.05

Accomplishments to Date

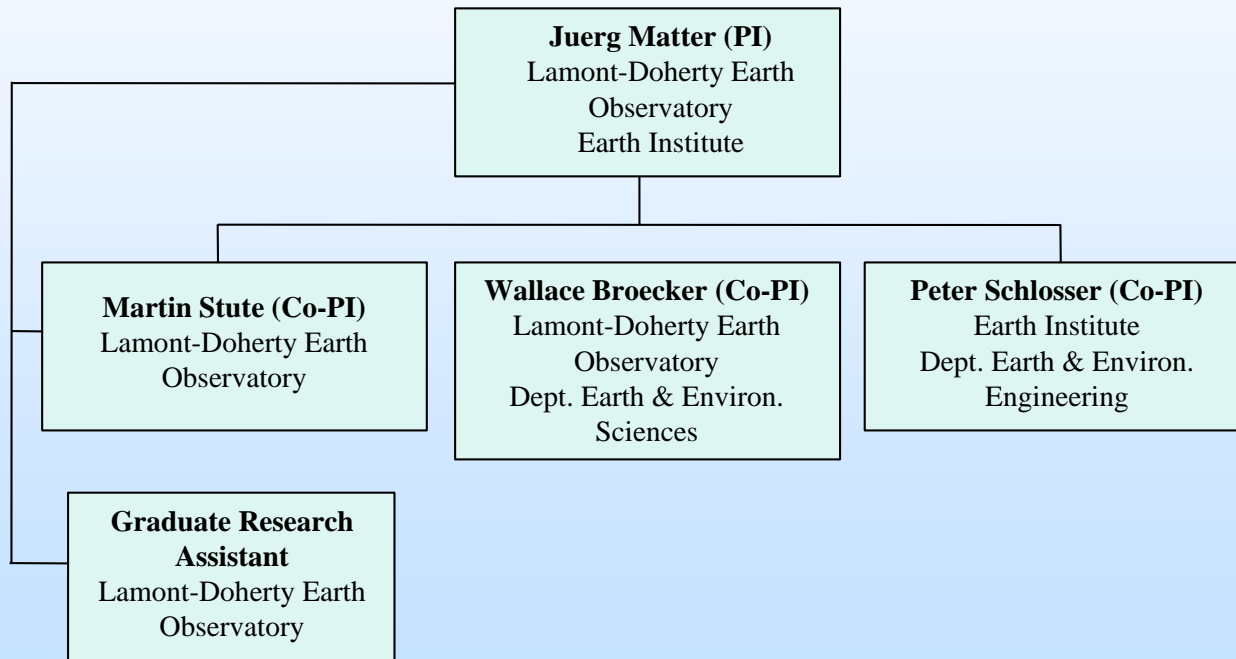
- Pure CO₂ injection (Phase I) was successfully completed.
- The mixed gas CO₂+H₂S injection (Phase II) was conducted for 6 months. Injection finalized due to wellbore clogging (biofilm and mineralization).
- Continuous collection of fluid and gas samples for chemical and tracer analyses is being conducted in injection and monitoring wells for Phase I and Phase II injection.
- Successful monitoring and verification of subsurface CO₂ mineralization along the flow path from injection to monitoring well by using ¹⁴C_{DIC} as a reactive tracer.
- Positive proof of subsurface CO₂ mineralization in monitoring well by secondary carbonate minerals with elevated (above modern carbon) ¹⁴C/¹²C ratios.
- Drilling of 600m hole into formation currently going on, coring planned for fall of 2014

Summary

- Preliminary analysis of the tracer data from the Phase I (pure CO₂ injection) indicates CO₂ mineralization via CO₂-fluid-basalt reactions.
- Mass balance calculation reveals that over 90% of the injected CO₂ has been mineralized within less than a year.
- The developed and applied tracer techniques are successful surveying tools for dissolved and chemically transformed CO₂, leading to a quantification (mass balance) of stored CO₂ in geologic reservoirs.

Appendix

Organization Chart



Gantt Chart

Tasks	BP I					BP II								BP III			
	Qt1	Qt2	Qt3	Qt4	Qt5	Qt1	Qt2	Qt3	Qt4	Qt5	Qt6	Qt7	Qt8	Qt1	Qt2	Qt3	Qt4
Task 1.0 Project Management, Planning and Reporting							E					J					
Task 2.0 Monitoring the CO₂ movement with SF₅CF₃ in the basalt formation							E					J					
Subtask 2.1 Monitoring the SF ₅ CF ₃ concentration in target injection interval and overlying shallow aquifer		A						F		I				M			
Subtask 2.2 SF ₅ CF ₃ Data Analysis			C					G		I				M			
Task 3.0 Monitoring of geochemical reactions and in situ mineral carbonation with ¹⁴C							E					J					
Subtask 3.1 Monitoring the ¹⁴ C concentration in target injection interval and overlying shallow aquifer			B					F		I				M			
Subtask 3.2 Carbon-14 and d ¹³ C Analysis					D			G		I			K	M			
Task 4.0 Mineral carbonation studies on core samples																	
Subtask 4.1 Wireline core drilling																	
Subtask 4.1.1 Drilling plan								H					L				
Subtask 4.1.2 Drilling and coring															N		
Subtask 4.2 Mineralogical and geochemical analysis of core samples																O	
Task 5.0 Quantification of mineral carbonation in the CarbFix basalt storage reservoir																P	

- Delay in completion of drilling core hole because of drill rig availability

Bibliography

- Journal, multiple authors:

Matter, JM, Broecker, W, Gislason, S, Gunnlaugsson, E, Oelkers, E, Stute, M, Sigurdardottir, H, Stefansson, A, Wolff-Boenisch, D, Axelsson, G, Sigfusson, B (2011), The CarbFix Pilot Project – storing carbon dioxide in basalt. *Energy Procedia* 4, 5579-5585.

Sigfusson, B, Gislason, SR, Matter, JM, Stute, M, Gunnlaugsson, E, Gunnarsson, I, Aradottir, ES, Mesfin, K, Alfredsson, HA, Wolff-Boenisch, D, Arnarson, MT, Oelkers E (2014), Injection of dissolved CO₂ into the subsurface: a novel carbon storage method. *International Journal of Greenhouse Gas Control* (in review).